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FLUORIDE AT THE NORTH BOUNDARY OF ROCKY MOUNTAIN ARSENAL

A Report
by
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FLUORIDE AT THE NORTH BOUNDARY OF ROCKY MOUNTAIN ARSENAL

1. Purpose and Scope

The purpose of this report is to calculate groundwater flow and fluoride mass flux at the north boundary of Rocky Mountain Arsenal. The calculations were done for the existing bentonite barrier and the extensions of it to the east and to the west. Figure 1 shows the area studied. Both alluvial and Denver formation aquifers are considered.

2. Discussion

a. Alluvial Aquifer

(1) The mean fluoride values listed in Table 1 are based upon two or more observations except as indicated. The number of wells used in each zone varies because of the distribution of wells in the area.

(2) The saturated thickness of the alluvial aquifer is based upon the review of stratigraphic cross-sections in the north boundary area. Permeability was estimated from pump tests conducted by the Waterways Experiment Station in 1978 and from calculations done in a report by S. P. Miller of Waterways Experiment Station.[1] The hydraulic gradient was determined from a Rocky Mountain Arsenal water table elevation map.

(3) Table 2 shows that seventy-one percent of the alluvial water flowing across the north boundary is in zones 4 and 5. The fluoride level in zone 4 is only 0.02 mg/l above the State of Colorado's maximum limit for fluoride in drinking water. That in zone 5 is less than half of the maximum drinking water limit. These two zones represent thirty-six percent of the barrier length but over seventy percent of the water flow.

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[1] Miller, S.P., Interim Containment System Groundwater Treatment, Rocky Mountain Arsenal, Denver, CO, USAE, Waterways Experiment Station, Soils and Pavements Laboratory, September, 1976.

SECTION 23

Well ID	Bore ID	Barrier Zone	$\overline{XF^-}$	Depth
41	390	1	4.56	15.4
1	25	1	5.13	8.1
OP306	-	1	4.53	-
125	260	1	*4.80	18.0
42	391	1	*1.17	16.8
124	259	1	*3.80	16.0
20	199	**2	*1.07	-
110	691	2	3.59	16.0
111	692	2	3.79	19.0
123	687	2	4.30	20.0
118	682	2	5.60	13.5
119	683	2	2.72	14.0
120	684	2	2.66	13.5
48	397	2	3.29	17.9

SECTION 24

Well ID	Bore ID	Barrier Zone	$\overline{XF^-}$	Depth
56	688	2	3.99	21.0
12	183	2	3.18	-
6	60	3	3.23	12.8
25	221	3	3.48	12.0
13	209	3	2.58	13.7
5	45	4	2.68	6.1
60	190	4	*2.40	18.4
61	191	4	2.42	17.0
59	344	4	2.41	18.0
29	345	4	2.20	20.3
4	119	5	1.42	9.0
30	347	5	1.08	19.4
31	349	5	0.89	20.4
32	351	6	0.27	44.7

*One Sample
**Existing Barrier Zone

TABLE 1

List of wells used to determine F concentration in the bentonite barrier zones of Sections 23 and 24 of Rocky Mountain Arsenal. Fluoride values are in mg/l. Depths are in feet.

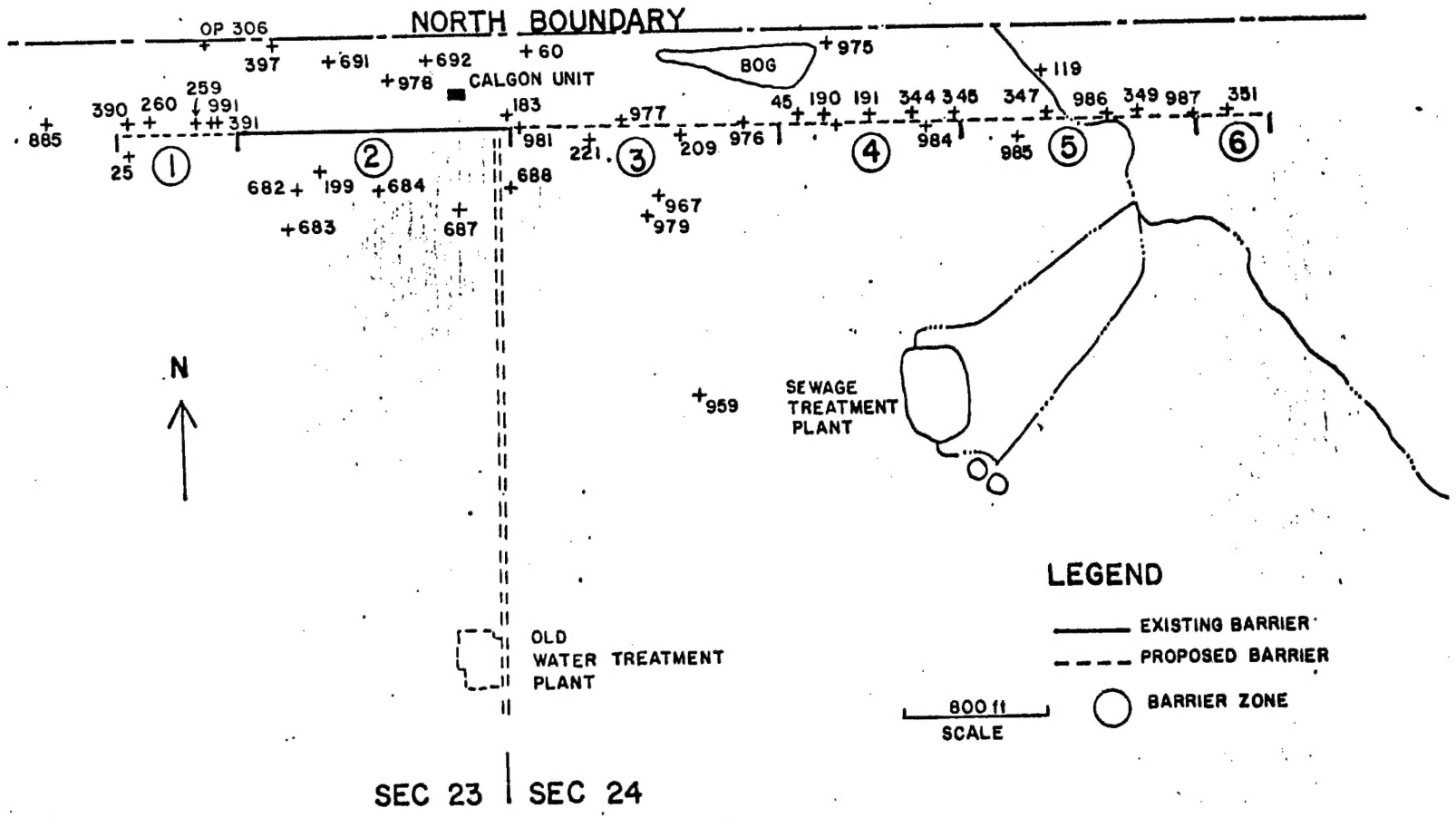

FIGURE 1

Area of Study in Sections 23 and 24 of Rocky Mountain Arsenal.
For clarity, only wells included in the study are shown.

By reducing the flow of water in zones 4 and 5 by 20, 40, 60 and 80 percent, fluoride mass flux changes according to Table 3.

Barrier Zone	1	**2	3	4	5	6	Totals
L ft	700	1500	1500	1000	1300	400	6400
M ft	7	7	10	10	15	10	
A ft^2	4900	10500	15000	10000	19500	4000	63900
K ft/da	200	200	200	575	575	200	
i	0.0067	0.0067	0.0067	0.0067	0.0067	0.0067	
Q ft^3/da	6566	14070	20100	38525	75124	5360	1.597×10^5
Q gal/da	49114	105244	150348	288167	561928	40092	1.195×10^6
Q gal/min	34.1	73.1	104.4	200.1	390.2	27.8	830
$\overline{XF^-}$ mg/l	3.18	3.42	3.10	2.42	1.13	*0.27	***1.90
$\overline{XF^-}$ g/gal	0.012	0.013	0.012	0.009	0.004	0.001	
F g/da	589	1368	1804	2594	2248	40.9	8644

L = length of aquifer
M = thickness of aquifer
A = L·M - cross sectional area
K = permeability
I = hydraulic gradient
Q = K·A·i - flow
$\overline{XF^-}$ = mean value of F^- concentration
F = Q·$\overline{XF^-}$ - mass flux

* One Sample
** Existing Barrier Zone
*** QTotal/FTotal - $\overline{XF^-}$ Total

TABLE 2

Calculations for water flow and mass flux of F^- for each bentonite barrier zone of the alluvial aquifer

Percent Reduction	Q gal/da (gal/min)	F g/da (g/min)	$\overline{XF^-}$ mg/gal (mg/l)
20	1.025×10^6 (712)	7675 g/da (5.32)	7.5 (1.98)
40	8.550×10^5 (594)	6707 g/da (4.66)	7.8 (2.06)
60	6.849×10^5 (476)	5738 g/da (3.98)	8.4 (2.22)
80	5.151×10^5 (358)	4770 g/da (3.31)	9.3 (2.46)

TABLE 3

Changes in mass flux and concentration of F^- at the north boundary of Rocky Mountain Arsenal by reducing water flow through the high permeability zones of the bentonite barrier extension.

The effect upon fluoride level decreasing flow in the zones of high permeability is shown by Figure 2.

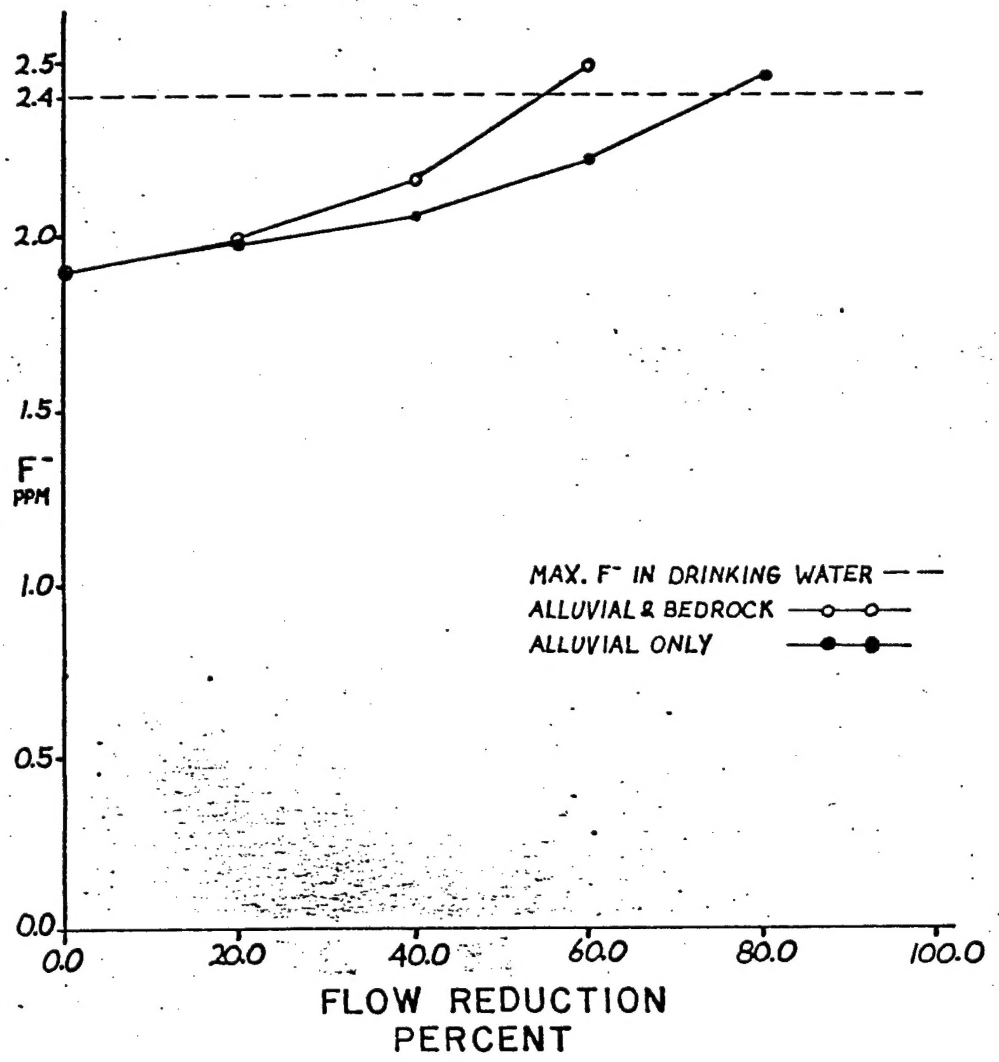

FIGURE 2

Reduction of maximum flow required to produce a fluoride concentration in excess of the maximum state limit.

b. Denver Formation

(1) The mean fluoride concentrations in the Denver sands are well below the maximum state limit. Of twenty-six sites sampling water in the Denver Formation, only two exceed 2.40 mg/l. The fluoride values shown in Table 4 are used to create the mean fluoride values used in Table 5.

Site ID	Well ID	Depth Ft	$\overline{XF^-}$	Barrier Zone
885S	23-163	46.5	0.37	1
885D	23-164	85.0	1.98	1
991S	23-167	49.5	*0.34	1
991M	23-168	71.5	**5.10	1
991D	23-169	94.0	1.18	1
978S	23-161	69.0	0.83	2
978D	23-162	107.5	0.54	2
959	24-113	41.0	2.30	3
967	24-129	25.2	**2.46	3
976S	24-131	62.2	0.69	3
976D	24-132	50.5	1.05	3
977S	24-133	48.0	1.01	3
977D	24-134	73.5	1.24	3
979S	24-135	33.0	1.81	3
979M	24-136	57.5	0.62	3
979D	24-137	90.5	1.21	3
981S	24-138	43.0	1.66	3
981D	24-139	79.0	1.16	3
983S	24-140	27.5	2.24	4
983D	24-141	62.5	1.74	4
984S	24-142	49.0	1.58	4
984D	24-143	75.0	2.23	4
985	24-144	49.0	1.08	5
986S	24-145	57.0	1.21	5
986D	24-146	37.5	1.30	5
987	24-147	82.5	1.28	5

*One sample
**Exceeds State Limit

TABLE 4

Sites at the north boundary of Rocky Mountain Arsenal sampling groundwater from the Denver formation in Sections 23 and 24. Mean fluoride concentrations, $\overline{XF^-}$, are in mg/l(ppm).

(2) The calculations in Table 5 are based upon the cross-sectional area of Denver sand fifty feet or less below ground surface. This was done because the preliminary design idea for the extension of the treatment system was to construct it to an average depth of fifty feet.

(3) The permeability of sand units in the Denver formation is two orders of magnitude less than that of the alluvial aquifer. This is based upon a core analysis from Boring 978 of a sand unit at a depth of 110 feet with a laboratory permeability of 2640 millidarcys (7.2 ft/da).

(4) Boring 975, located at the east end of "Bog", indicates that the regional dip of the Denver formation is to the north. The normal regional dip of the formation is to the south in the vicinity of Rocky Mountain Arsenal. Since the sand units in the formation are completely confined by shale and clay, the hydraulic gradient and the regional dip are the same. The hydraulic gradient shown in Table 5 is roughly twice that of the alluvial aquifer.

(5) It can be seen from Table 6 that mass flux of fluoride in Denver sands represents only about one percent of the total mass flux of fluoride at the north boundary of Rocky Mountain Arsenal. The total area of bedrock sand mapped along the bentonite barrier alignment is 1,333, 123 square feet. The vertical distribution of Denver sand is shown in Table 7.

(6) Table 8 shows that total groundwater flow in the north boundary area must be reduced by just over half the maximum amount before the fluoride concentration exceeds the maximum state limit.

Barrier Zone	1	2	3	4	5	Totals
A ft^2	10700	4660	4760	5660	11960	37740
K ft/da	7.2	7.2	7.2	7.2	7.2	
i	0.0114	0.0114	0.0114	0.0114	0.0114	
Q ft^3/da	878	382	391	465	982	3099
Q gal/da	6567	2857	2925	3478	7345	23173
Q gal/min	4.56	1.99	2.03	2.41	5.10	16.1
$\overline{XF^-}$ mg/l	0.36	1.24	1.12	1.91	1.15	1.04
$\overline{XF^-}$ g/gal	0.0013	0.0047	0.0042	0.0072	0.0043	0.0039
F g/da	8.54	13.4	12.3	25.0	31.6	90.8

TABLE 5

Calculations for water flow and mass flux of F^- for each bentonite barrier zone in Denver sand. There are no wells in Zone 6 that sample Denver sand.

Barrier Zone	1	2	3	4	5	6	Total F
F g/da alluvial	589	1368	1804	2594	2248	40.9	8644
F g/da bedrock	8.54	13.4	12.3	25.0	31.6	-	90.8
F g/da total	597.5	1381.4	1816.3	2619	2279.6	40.9	8734.8
% F alluvial	98.6	99.0	99.3	99.0	98.6	-	
% F bedrock	1.4	1.0	0.7	1.0	1.4	-	

TABLE 6

Comparison of fluoride mass flux in the alluvial and bedrock aquifers in different bentonite barrier zones.

Depth Feet	Area	Percent Area
<50	40520	30%
>50	92603	70%

TABLE 7

Vertical distribution of sands in the Denver formation at the north boundary of Rocky Mountain Arsenal, Sections 23 and 24.

Percent Q	Q, gal/min	Q, gal/da	F, g/da	C, mg/gal	C, mg/l
100	846	1.218×10^6	8735	7.2	1.90
80	677	9.753×10^5	7352	7.5	1.99
60	509	7.324×10^5	5968	8.2	2.16
40	340	4.894×10^5	4583	9.4	*2.48
20	171	2.466×10^5	3197	13.0	3.43

*Exceeds maximum state limit

TABLE 8

Groundwater flow and mass flux of fluoride at the north boundary of Rocky Mountain Arsenal combining alluvial and bedrock groundwater. C is concentration of F^-

c. Fluoride Data

(1) The reliability of mass flux calculations is based largely upon the quality of analytical data for fluoride concentration in groundwater. Historically, fluoride data produced by the MALD at Rocky Mountain Arsenal shows higher values than those produced by the Colorado Department of Health. This difference in analytical values is illustrated in a Memorandum for Record from USATHAMA:

> "As fluoride data was evaluated at each well location, it was apparent that duplicate analyses were conducted for the period 1 Jul 75 to 15 Jan 76. The first was performed by the State of Colorado at the same time a second was performed by MALD, RMA. Visual comparison indicated that consistently different results had been obtained. Table 3 represents a statistical comparison of the two sets of analyses. In every case the State of Colorado average is below that obtained by RMA. The difference is approximately 0.3 to 0.4 mg/l. Variation between the two results can probably be related to a difference in the analytic measurement technique. Comparison of the variance indicates that in almost every case, the dispersion of results is greater for RMA. Again, this anomally can be attributed to a difference in analytical measurement techniques."[2]

(2) Table 3 from the same Memorandum for Record is presented as Table 9 in this report for visual comparison of the fluoride analytical techniques of Rocky Mountain Arsenal and the Colorado Department of Health.

(3) While working at the Analytical Systems Branch, Bldg 743, Rocky Mountain Arsenal, the writer conducted an informal study to find out if fluoride concentration in water was dependent upon analytical technique. The established technique, a colorimetric one with a distillation step, was compared to three techniques using an ion specific electrode (ISE) detector. The study was done using actual 360° Program wells and fluoride standards in distilled water. The study indicated that fluoride concentration in the same sample varied according to the analytical technique used. The technique comparison study is presented as Table 10.

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[2]Campbell, D. L., DRCPM-DRR, MFR, 1 February 1978, Evaluation of RMA Fluoride Data.

TABLE 9[3]

Comparison of Fluoride Analysis Techniques[1]

New Well No.	Old Well No.	Performing Lab[2]	No. of Data Points	Average Concentration[3] ($\bar{X}$)	Variance[3] (σ^2)	Difference[4] In Averages ($\Delta\bar{X}$)	Difference In Variance[5] ($\Delta\sigma^2$)
			NORTH BOUNDARY VICINITY				
23005	121	CH	9	2.700	0.046	+0.610	+ 1.290
		RM	15	3.310	1.336		
24006	60	CH	9	2.878	0.042	+0.520	+ 0.66
		RM	15	3.398	0.702		
24004	119	CH	6	1.800	0.013	+0.157	+ 0.023
		RM	7	1.957	0.036		
23001	25	NO DUPLICATE ANALYSES PERFORMED					
24005	45	CH	8	2.275	0.294	+0.296	− 0.277
		RM	8	2.571	0.0167		
23009	75	CH	9	4.289	0.063	+0.363	+ 0.804
		RM	14	4.652	0.867		
23004	115	CH	8	3.988	0.046	+0.378	+ 0.226
		RM	13	4.366	0.272		
24001	122	CH	9	2.766	0.020	+0.365	+ 0.110
		RM	13	3.132	0.130		
			NORTHWEST BOUNDARY VINICITY				
22004	105	CH	8	7.713	0.918	+0.402	- 0.274
		RM	8	8.115	0.644		
22005	108	NO DUPLICATE ANALYSES PERFORMED					

NOTES:
[1] Time interval includes 75148 to 76013 (1 Jul 75 to 15 Jan 76)
[2] CH - State of Colorado, RM - Rocky Mountain Arsenal
[3] Expressed in mg/l.
[4] $\bar{X}$ (RMA) - $\bar{X}$ (State of Colorado)
[5] σ^2(RMA) - σ^2(State of Colorado)

LE 9 (Continued)

New Well No.	Old Well No.	Performing Lab[2]	No. of Data Points	Average Concentration[3] ($\bar{X}$)	Variance[3] (σ^2)	Difference[4] In Averages ($\Delta\bar{X}$)	Difference In Variance ($\Delta\sigma^2$)
NORTHWEST BOUNDARY VICINITY (Continued)							
22003	104	CH	11	2.673	0.029	+ 0.152	- 0.017
		RM	11	2.825	0.012		
27001	103	CH	9	0.717	0.004	+ 0.074	- 0.002
		RM	9	0.791	0.002		
NORTH BASIN F VICINITY							
23002	71	NO DUPLICATE ANALYSES PERFORMED					
23006	132	CH	10	2.760	0.086	+ 0.340	+ 0.103
		RM	15	3.100	0.189		
23007	133	CH	10	2.420	0.029	+ 0.432	+ 0.182
		RM	15	2.852	0.211		
23008	134	CH	10	2.650	0.066	+ 0.616	+ 0.074
		RM	15	3.266	0.140		
26008	118	CH	10	2.770	0.152	+ 0.175	+ 0.020
		RM	10	2.945	0.174		
26007	73	CH	9	1.811	0.017	+ 0.289	+ 0.008
		RM	14	2.100	0.025		

Table 9

Comparison of fluoride techniques of Rocky Mountain Arsenal and the Colorado Department of Health.[3]

[3] Ibid

(4) Both studies show that fluoride values vary according to the technique used. Specifically, the Colorado Department of Health has produced values 0.3 - 0.4 mg/l lower than those produced by the Analytical Systems Branch, Bldg 743, Rocky Mountain Arsenal, for the same sites. Viewing Table 11 with this in mind, one sees that flow must be reduced to less than forty percent of maximum before the 2.4 mg/l maximum limit of fluoride is exceeded.

Sample	Site ID	Colorimetric w/Distillation	ISE (CDTA) w/Distillation	ISE w/CDTA	ISE No CDTA
A01621	20-1	1.49	1.60	1.29	1.24
A01622	6-1	1.07	1.25	0.90	0.90
A01623	6-2	1.73	1.84	1.56	1.56
A01624	7CDDC	2.32	2.46	1.96	1.94
A01625	30BCCD	1.58	1.75	1.42	1.41
A01626	26CDBA	1.99	2.51	1.79	1.80
A01627	35-5	1.11	1.40	1.00	0.98
A01628	26-1	3.50	3.58	2.92	2.86
A01629	26-5	2.12	2.54	1.82	1.70
A01630	27-2	1.40	1.58	1.23	1.22
A01637	22-2	0.45	0.77	0.35	0.35
A01662	26-19	3.56	3.75	3.02	2.96
A01663	26-21	2.60	2.95	2.22	2.20
A01664	26-22	2.76	3.24	2.48	2.40
A01665	26-31	0.91	1.16	0.78	0.77
$\bar{X}$2.0STD		2.00	2.02	2.00	2.00
$\bar{X}$1.5STD		1.58		1.54	
$\bar{X}$1.0STD				*1.06	
$\bar{X}$0.5STD		0.58		0.54	0.54
$\bar{X}$0.2STD			0.20		0.20

*One Sample

TABLE 10

Comparison of fluoride determination techniques (23 February 1978). Fluoride values are in mg/l (ppm). CDTA is a reagent that prevents fluoride ions from becoming complexed with metal ions.

Fluoride Method	% Maximum Flow to Exceed 2.4 mg/l	Q, gpd (gpm)
RMA	44.4	5.045×10^5 (375)
CDH	35.6	4.334×10^5 (301)

TABLE 11

Comparison of fluoride methods in relation to groundwater flow at the north boundary.

3. Conclusions

a. Although nearly eighty percent of the alluvial wells used in this report exceed the 2.4 mg/l fluoride limit, their effect is more than offset by the low values found in barrier zones 4 and 5. This off-setting effect is due to higher permeability in those two zones, which results in higher water flow rates.

b. If fluoride were the only ion to be considered in the extension of the north boundary treatement system, the eastern end of it could be located in the vicinity of Well 24-29 (boring 345). However, chemical data shows that Nemagon (DBCP) is found in wells east of 24-29.

c. Since the treatment system would have to be extended to First Creek to intercept Nemagon contamination, fluoride is eliminated as a contaminant in the groundwater. The additional water containing Nemagon has fluoride levels less than one-half of the maximum fluoride limit. When this water is mixed with that from other areas of the north boundary containing higher fluoride concentration, dilution occurs. Thus, fluoride concentration of water entering the treatment plant is well below the maximum limit of 2.4 mg/l.

4. Recommendations

a. The treatment system should be extended eastward as planned to a point just east of Well 24-32 (Boring 351). By extending the system to this point, it is highly probable that both Nemagon and fluoride will be eliminated as groundwater contaminants at the north boundary of Rocky Mountain Arsenal. This is based upon current chemical data.

b. It is recommended tha a fluoride treatment module not be installed in the expanded treatment system. However, the system should include plumbing connections so that a fluoride module could be easily installed if subsequent chemical data showed the need for one.

c. Recent chemical data indicates that several organic compounds may be in Denver sand at depths greater than the fifty foot design depth of the expanded north boundary treatment system. upon completion of sampling and evaluation of chemical data from the north boundary area, a recommendation about the depth of the proposed treatment system can be made.